

# Spin-zero anomaly in the magnetic quantum oscillations of a two-dimensional metal

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We report on an anomalous behavior of the spin-splitting zeros in the de Haas-van Alphen (dHvA) signal of a quasi-two-dimensional organic superconductor. The zeros as well as the angular dependence of the amplitude of the second harmonic deviate remarkably from the standard Lifshitz-Kosevich (LK) prediction. In contrast, the angular dependence of the fundamental dHvA amplitude as well as the spin-splitting zeros of the Shubnikov-de Haas signal follow the LK theory. We can explain this behavior by small chemical-potential oscillations and find a very good agreement between theory and experiment. A detailed wave-shape analysis of the dHvA signal corroborates the existence of an oscillating chemical potential.

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For three-dimensional (3D) metals the well-established theory of Lifshitz and Kosevich (LK) [1] can comfortably be utilized to obtain highly valuable band-structure parameters [2]. The LK theory is well proven and has the advantage of easy applicability to the experimentally measured magnetic quantum oscillations. The situation is considerably less resolved for two-dimensional metals. Both analytical [3] as well as numerical [4] models have been developed which were proven valid somewhat later by experiments (see [5, 6] and references therein). However, in these models not all aspects have been taken into account and they are not as easily applicable as the LK theory. In addition, not all band-structure parameters can be extracted satisfactorily from the existing theories leaving some experimental features unexplained.

Prototypical examples for which the fundamental theoretical predictions can be tested are the quasi-two-dimensional (2D) organic metals based, e.g., on the organic donor BEDT-TTF (= bisethylenedithio-tetrathiafulvalene or ET for short). The dHvA signal in these layered metals is usually easy to detect and it is mostly comprised by only a small number of oscillation frequencies [7]. Consequently, the Fermi surfaces are relatively simple and in most cases highly two dimensional, i.e., with negligible dispersion perpendicular to the conducting planes. Nevertheless, in dHvA signals only seldom notable deviations from the 3D LK theory appeared [8].

This is remarkably different for the organic superconductor  $\beta''$ -(BEDT-TTF)<sub>2</sub>SF<sub>5</sub>CH<sub>2</sub>CF<sub>2</sub>SO<sub>3</sub> which shows a dHvA signal almost perfectly in line with that expected for an ideal 2D metal with fixed chemical potential [5]. However, some questions remain. That is, in order to fix the chemical potential either an unusually large additional electronic density of states (DOS), originating from a different band, has to be assumed [5] or some localized states were proposed to be responsible [9]. In addition, although the dHvA signal could be described extraordi-

narily well by theory [5] small deviations still are visible (see Fig. 2 below) [10]. Here, we prove this latter feature to be valid by careful additional measurements utilizing the modulation-field technique. We further report on an unusual angular dependence of the spin-splitting zeros of the second harmonic. As we will show explicitly, both effects reflect the existence of small oscillations of the chemical potential. Especially the spin-zero anomaly of the second harmonic, therefore, offers a definite way to validate these oscillations.

We discuss here results of dHvA experiments that have been described in detail previously [5, 11]. Different high-quality  $\beta''$ -(BEDT-TTF)<sub>2</sub>SF<sub>5</sub>CH<sub>2</sub>CF<sub>2</sub>SO<sub>3</sub> single crystals have been measured by use of a capacitance cantilever torquemeter down to about 0.4 K as well as utilizing the modulation-field technique down to ~30 mK. The crystals were grown by electrocrystallization at Argonne National Laboratory [12].

For  $\beta''$ -(BEDT-TTF)<sub>2</sub>SF<sub>5</sub>CH<sub>2</sub>CF<sub>2</sub>SO<sub>3</sub>, the dHvA signal consists of only one frequency  $F = F_0 / \cos(\Theta)$ , where  $F_0 = (198 \pm 1)$  T is the dHvA frequency at  $\Theta = 0$ , i.e., for magnetic field applied perpendicular to the highly conducting plane [5, 11]. One of the puzzling results we discuss here, is the unusual angular dependence of the second harmonic,  $A_2$ , of the dHvA signal (Fig. 1) that does not follow the behavior predicted by the LK theory (dashed line in Fig. 1). On the other hand, the fundamental amplitude,  $A_1$ , is completely in line with expectation. To be more precise, the dHvA amplitudes in the 2D LK theory are given by

$$A_p = M^0 p^{-1} R_T(p) R_D(p) R_S(p), \quad (1)$$

where the prefactor  $M^0 = \frac{eA}{2\pi^2\hbar} \frac{S(\varepsilon_F)}{m^*}$  is given by the Fermi-surface area  $S(\varepsilon_F)$  and the effective cyclotron mass  $m^*$ ,  $e$  is the electron charge,  $A$  the sample area,  $p$  counts the harmonics, and  $R_T(p)$ ,  $R_D(p)$ ,  $R_S(p)$  are the

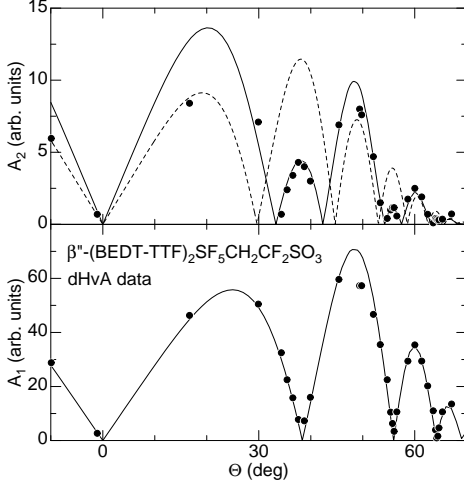


FIG. 1: Angular dependence of the fundamental ( $A_1$ ) and of the second harmonic ( $A_2$ ) of the dHvA signal of  $\beta''$ -(BEDT-TTF) $_2$ SF $_5$ CH $_2$ CF $_2$ SO $_3$ . The solid lines are obtained by use of (8) and (9) assuming an oscillating chemical potential. For  $A_1$  the same result as in the LK theory is obtained. The dashed line is the behavior of  $A_2$  expected from the LK theory.

usual damping factors [2]. The term dominating the angular dependence is the spin-splitting factor given by  $R_S(p) = \cos[\frac{1}{2}p\pi g(m^*/m_e)]$ , where  $g$  is the electron  $g$  factor and  $m_e$  is the free-electron mass. Since for the present superconductor  $m^*/m_e = (2.0 \pm 0.1)/\cos(\Theta)$ ,  $R_S(p)$  repeatedly becomes zero for those angles where the dHvA oscillations of the spin-up and spin-down electrons interfere destructively. This allows to determine  $gm^*/m_e = (3.92 \pm 0.01)/\cos(\Theta)$  from the vanishing of  $A_1$  quite accurately. The complete angular dependence of  $A_1$  of the torque signal [13] can be well described with a Dingle temperature  $T_D = 0.85$  K for the present sample at temperature  $T = 0.4$  K and magnetic field  $B = 14.7$  T (solid line in the lower panel of Fig. 1).

In spite of this successful application of the 2D LK theory for  $A_1$  it fails clearly to describe the angular dependence of  $A_2$  (dashed line in Fig. 1). Especially the spin-splitting zeros of  $A_2$  are expected at considerably different positions. Obviously, some of the assumptions used in the derivation of the 2D LK theory are not justified for the 2D metal investigated here. Indeed, it has been predicted that for 2D metals the spin factor  $R_S(2)$  may deviate strongly from the LK behavior [14]. Depending on the background DOS, i.e., the amplitude of chemical-potential oscillation,  $A_2$  should vanish at shifted angular positions. The predicted shift is, however, opposite to what we observe experimentally. That is, according to [14] the first zero of  $A_2$  should occur at smaller angle than given by the LK theory (dashed line in Fig. 1), the second zero at higher angle and so forth.

It is therefore worthwhile to look for another theoretical explanation. As was shown previously, the oscilla-

tions of the magnetization in 2D layered conductors and the oscillations of the chemical potential are closely related and mathematically described by similar (but not identical) series [15]. The oscillating part of the magnetization can be written as [16]

$$\tilde{M} = M^0 \text{Im} \sum_{p=1}^{\infty} \frac{(-1)^p}{p} \exp \left[ 2\pi i p \left( \frac{F}{B} + \frac{\tilde{\mu}}{\hbar\omega_c} \right) \right] \hat{R}(p), \quad (2)$$

with  $F = S(\varepsilon_F)/(2\pi e\hbar)$ , the cyclotron frequency  $\omega_c = eB/m^*$ , and  $\hat{R}(p) = I(p)R_T(p)R_S(p)R_D(p)$ . The factor  $I(p)$  takes account of interlayer electron-hopping effects which are beyond the LK theory [17]. The oscillating part of the chemical potential,  $\tilde{\mu} = \mu - \varepsilon_F$ , is given by

$$\tilde{\mu} = \hbar\omega_c \text{Im} \sum_{p=1}^{\infty} \frac{(-1)^p}{\pi p} \exp \left[ 2\pi i p \left( \frac{F}{B} + \frac{\tilde{\mu}}{\hbar\omega_c} \right) \right] \hat{R}(p). \quad (3)$$

The consequences of  $\tilde{\mu} \neq 0$  can be realized by considering the oscillating correction to  $\mu$  in lowest order

$$\mu = \varepsilon_F - \eta \sin \left( 2\pi \frac{F}{B} \right). \quad (4)$$

We assume here that  $\eta = \hbar\omega_c \hat{R}(1)/\pi \ll 1$  is a small real parameter. Using the notations  $z_p = 2\pi p F/B$ ,  $\eta_p = 2\pi p \eta/\hbar\omega_c$ , and the identity

$$\exp(-i\eta_p \sin z_1) = \sum_{n=-\infty}^{\infty} (-1)^n J_n(\eta_p) \exp(iz_n), \quad (5)$$

where  $J_n(\eta_p)$  is the Bessel function of order  $n$ , one can write the magnetization (2) in the standard form

$$\tilde{M} = \sum_{n=1}^{\infty} A_n \sin \left( 2\pi n \frac{F}{B} \right). \quad (6)$$

The amplitudes of the harmonics are given by

$$A_n = M^0 \sum_{p=1}^{\infty} \frac{(-1)^p}{p} \hat{R}(p) [J_{p+n}(\eta_p) - J_{p-n}(\eta_p)]. \quad (7)$$

The amplitudes  $A_n$  are, therefore, weighted sums of the terms  $\hat{R}(p)$ . Contrary to the LK theory the latter term contains the additional factor  $I(p)$  that takes into account such effects as interlayer hopping [15, 17] or the dispersion of magnetic-breakdown bands [18]. (For  $\beta''$ -(BEDT-TTF) $_2$ SF $_5$ CH $_2$ CF $_2$ SO $_3$  magnetic breakdown is irrelevant as shown by measurements up to 60 T [19].) Important consequences of (7) are deviations from the usual LK temperature and magnetic-field dependences. This is realized, e.g., in the effective masses which apparently become smaller for each higher harmonic when extracted by use of the LK formula [2]. In the present case, an apparent effective mass of only about  $1.5 m_e$  is obtained for the second harmonic.

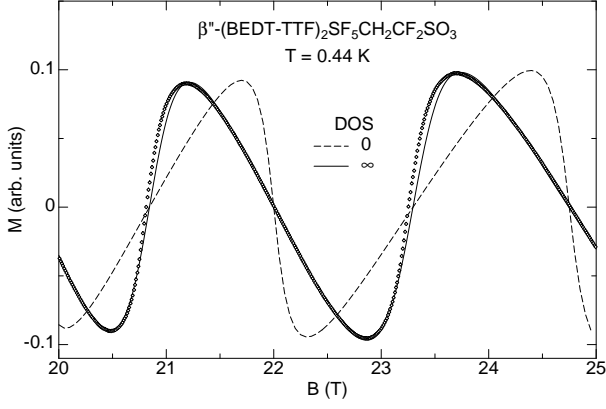


FIG. 2: Comparison of the measured dHvA data (open symbols) with the calculated signals for a 2D metal with fixed number of charge carriers (dashed line) and for a 2D metal with fixed chemical potential (solid line).

What is of importance here, is that the angular dependence, i.e., the spin-zero positions also differ from those predicted in the LK approach. To show this in more detail we consider the fundamental and second harmonic which can be compared to the experimental data. Since we assume  $\eta \ll 1$ , also  $\eta_1$  and  $\eta_2$  are small parameters. Accordingly, the relevant Bessel functions in (7) can be approximated as  $J_0(\eta_1) \approx J_0(\eta_2) \approx 1$  and  $J_1(\eta_1) \approx \eta_1/2 = \hat{R}(1)$  resulting in

$$A_1 = M^0 \hat{R}(1), \quad (8)$$

$$A_2 = -M^0 \left[ \frac{1}{2} \hat{R}(2) + \hat{R}(1)^2 \right]. \quad (9)$$

For a weakly oscillating chemical potential, therefore, the amplitude of the fundamental basically remains identical to the LK prediction, whereas  $A_2$  becomes a linear combination of the damping factors for  $p = 1$  and  $p = 2$ . Consequently, care has to be taken when extracting band-structure parameters from the second harmonic. Besides the modified temperature dependence (leading to the above mentioned apparent effective-mass peculiarities), an unusual angular dependence of  $A_2$  with shifted spin-splitting zeros results. The latter are determined by  $[\frac{1}{2} \hat{R}(2) + \hat{R}(1)^2] = 0$ . With  $R_D(1)^2 = R_D(2)$  and  $R_S(p)$  as stated above, the spin-splitting zeros are given by

$$\cos\left(\frac{\pi g m^*}{m_e}\right) I(2) + 2 \cos^2\left(\frac{\pi g m^*}{2 m_e}\right) \frac{R_T^2(1)}{R_T(2)} I^2(1) = 0. \quad (10)$$

Thus, the zeros are shifted as compared to the LK theory where the second term is absent. The shift is a weak function of temperature and magnetic field caused by the factors  $R_T(p)$  and  $I(p) = \int g(\varepsilon) \exp(2\pi i p \varepsilon / \hbar \omega_c) d\varepsilon$ . The layer-stacking factor for a simple cosine-like interlayer dispersion can be written as  $I(p) = J_0(\frac{4\pi t p}{\hbar \omega_c})$ , where  $t$  is the interlayer-hopping integral. For the present 2D superconductor there is no detectable dispersion across

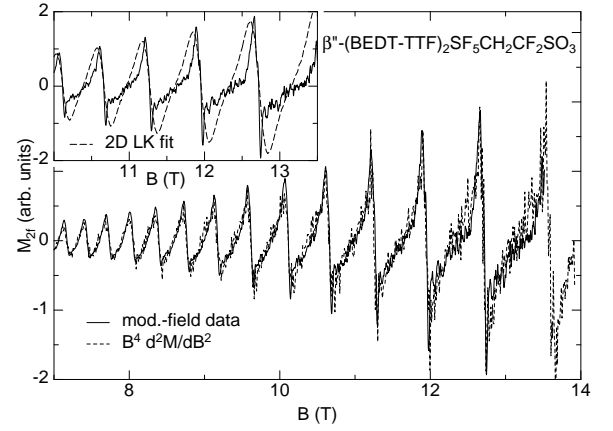


FIG. 3: Comparison of modulation-field dHvA data with the second derivative of magnetization data times  $B^4$  measured by the torque method. The inset shows the modulation-field data in comparison to the expected signal for a 2D metal with fixed chemical potential.

the layers and the DOS  $g(\varepsilon)$  associated with the electron hopping between the layers is unknown [20]. Nonetheless, because the hopping integral is very small compared to  $\hbar \omega_c$ ,  $I(p)$  may be approximated by 1.

The excellent agreement between our theory and experiment is evident from Fig. 1 where we used Eqs. (8) and (9) to obtain the solid lines. Since all experimental parameters,  $m^*$ ,  $T$ ,  $B$ , and  $T_D$ , are well known there is no free parameter except for simple scaling factors.

This result implies that a weak oscillation of the chemical potential exists. Indeed, when analyzing in detail the experimental dHvA wave shape small deviations from the 2D LK behavior for fixed chemical potential can be resolved. In Fig. 2 it is obvious that the observed steep increase of the dHvA signal cannot be described satisfactorily by the theoretical 2D LK behavior (solid line in Fig. 2). This corroborates the notion of an oscillating chemical potential. This oscillation, however, must be different from the usually predicted sawtooth-like 2D behavior [3] as visualized by the dashed line in Fig. 2.

Since possible artifacts, such as torque interaction, might obscure the dHvA signal we checked the validity of our torque result by comparing it with modulation-field data (Fig. 3). For a modulation-field amplitude not too large and signal detection on the second harmonic, the modulation-field data are approximately proportional to the second derivative of the magnetization with respect to  $B$  times  $B^4$  [2]. The excellent agreement between both signals is evident [21]. This proves the validity of both experimental data and verifies the deviation from the 2D LK behavior as real. Indeed, for the modulation-field data the deviation appears even more pronounced since the second derivative of  $M$  is analyzed (inset of Fig. 3).

Consequently, these results substantiate the existence of an oscillating chemical potential. This oscillation is

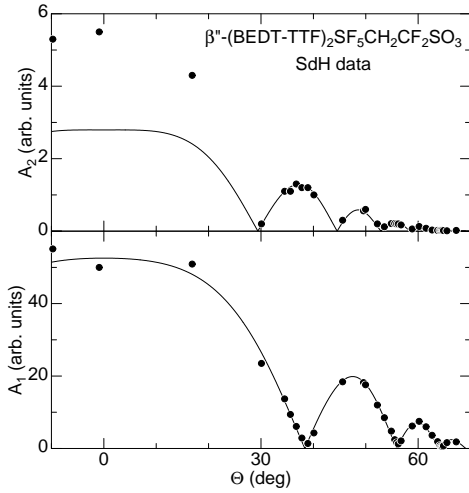


FIG. 4: Angular dependence of the fundamental ( $A_1$ ) and the second harmonic ( $A_2$ ) of the SdH signal. The solid lines show the expected behavior according to the 2D LK theory.

small, as assumed and realized by the minute wave-shape effects, but must be more elaborate than the simple lowest-order sinusoidal waveform considered in (4). Qualitatively, the waveform of  $\tilde{\mu}$  must be fast changing for rising  $M$  and slowly varying for decreasing  $M$ , similar as visualized in Fig. 1 of Ref. [4] for an almost fixed chemical potential. Indeed, the actual field dependence of the chemical-potential oscillations might be extractable by an iterative fitting procedure using Eqs. (2) and (3).

The final strong argument in favor for an oscillating chemical potential is the absence of any anomalous shifts of the spin-splitting zeros in the SdH signal (Fig. 4). Here, for the same parameters,  $T$ ,  $B$ , and  $T_D$ , as for the dHvA data in Fig. 1, the 2D LK theory describes the angular dependences of the SdH amplitudes very well (except for some  $A_2$  points close to  $\Theta = 0$ ). In particular, the zeros of the second harmonic lie exactly at the positions expected for a metal with fixed chemical potential. Obviously, the electrical leads, necessary for measuring the SdH signal, act as a charge-carrier reservoir leading to a constant chemical potential. It is noteworthy that for an (even with small amplitude) oscillating chemical potential of inverse-sawtooth shape split peaks in the SdH signal should occur [22]. In line with a fixed chemical potential for electrical-transport measurements, however, such split peaks do not occur in our SdH measurements.

In conclusion, we observed and explained quantitatively an anomalous angular dependence of the dHvA signal in a 2D metal. This is shown to be a genuine effect of the two dimensionality that can be utilized as a direct proof for an oscillating chemical potential. In the present case these oscillations are very small but directly visible in the detailed dHvA wave shape. In SdH experiments, no chemical-potential oscillations are detected which in

turn means that charge oscillates into and out of the sample during a SdH period.

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